February 21, 1861.

Major-General SABINE, R.A., Treasurer and Vice-President, in the Chair.

The following communications were read:—

I. "On Terephthalic Acid and its derivatives." By WARREN DE LA RUE, Ph.D., F.R.S. &c., and HUGO MÜLLER, Ph.D., F.C.S. Received February 7, 1861.

Whilst pursuing our investigation of Burmese naphtha, an abstract of which we have already communicated to the Society, we noticed, among the products of the action of nitric acid on certain liquid hydrocarbons contained in Rangoon tar, an acid of peculiar properties. A very lengthened investigation of this acid and its derivatives we are about bringing to a close; but as the drawing up of this account will necessarily occupy a considerable time, we have thought it desirable to send a short abstract of the chief results we have obtained, with the view of its appearing in the 'Proceedings' of the Society.

M. Caillot, about fifteen years ago, obtained a peculiar acid among the products of the action of dilute nitric acid on oil of turpentine, to which he gave the name of Terephthalic acid, on account of its generation from oil of turpentine and its isomerism with phthalic acid. M. Caillot's account of his new acid was so brief and incomplete, that, although we recognized many points of resemblance between it and the acid we had obtained from Burmese naphtha, we were compelled to repeat his experiments on oil of turpentine before we could fix with certainty the identity of the two products. In the course of these experiments, in which that identity was fully established, we noticed some interesting features in the compounds of the acid and the derivatives we discovered; more especially the relation of terephthalic acid to the well-known aromatic series,—a relation precisely analogous to that which succinic acid bears to the fatty acids. The close relation which exists between terephthalic acid and benzoic acid is most strikingly manifested in the great number of derivatives which are obtained from the former; indeed, nearly all of the most characteristic benzoyl-

compounds have their analogues amongst the derivatives of terephthalic acid. Terephthalic acid being a bibasic acid, maintains its character throughout its various transformations, and it is this fact which claims particular interest.

Terephthalic acid, as well as its derivatives, forms the first term of a new series of well-characterized bodies, and may, as such, be considered the prototype of a great number of compounds still unknown.

Without dwelling at present on the tedious process by which terephthalic acid is produced, we may mention that it is obtainable from various sources. We have, for instance, found that it is invariably formed, in a relatively small proportion, when toluylic acid is prepared from cymol; it is also formed when cymol is treated with fuming nitric acid for the purpose of preparing nitrotoluylic acid. It is important to mention, that whether the cymol be prepared from oil of cumin or from camphor, the result is the same.

Subsequently, we found that insolinic acid, which was described some years ago by Hofmann as a new acid of the formula $C^9 H^8 O^4$, is in reality terephthalic acid. The formation of this acid from oil of cumin or cuminic aldehyde by the action of chromic acid on these substances, turned out to be the most ready method of preparing terephthalic acid; and the principal part of our experiments were made with terephthalic acid which had been obtained from oil of cumin by this process.

Terephthalic acid being isomeric with phthalic acid, has the formula $C^8 H^6 O^4$ (Carbon=12, Oxygen=16), as already known. When pure, it forms a white opake powder; but if thrown down from a boiling dilute alkaline solution, it may be obtained in a crystalline state. When collected on a filter, these crystals dry in paper-like masses of a silky lustre. Terephthalic acid is not perceptibly soluble in ether, chloroform, acetic acid, water, or the other usual solvents. Concentrated sulphuric acid dissolves it to a considerable extent, especially when warm, without the formation of sulpho-terephthalic acid, and the acid separates unchanged on the addition of water. On heating, terephthalic acid sublimes without previously fusing. The sublimate, which is indistinctly crystalline, has the same composition and properties as the original acid, and therefore, unlike other bibasic acids, terephthalic acid cannot be converted into an anhydrite by merely heating it. Terephthalic

acid exhibits a remarkable deportment with regard to its salts; for although bibasic, there appear to exist no double salts; and even acid salts are only prepared with the greatest difficulty.

The alkaline terephthalates are all very soluble in water, but are insoluble in alcohol. The potassium, sodium, and ammonium compounds can be obtained in well-crystallized forms. Calcium and barium salts are less soluble than the before-named, and may be obtained in small scaly crystals. The copper salt is a pale blue crystalline powder. The silver and the lead salt occur as curdy precipitates when obtained by double decomposition. The compounds of terephthalic acid with the alcohol radicals possess a particular interest, as they furnish the most direct proof of the bibasic nature of the acid. There exist neutral and acid compounds. The neutral ethers are obtained either by the action of chloride of terephthalyl on the alcohols, or by means of the iodide of the alcohol radicals and terephthalate of silver or of potassium.

The methyl-terephthalic ether, $C^8 H^4 (CH^3)^2 O^4$, is the most characteristic compound, and consequently may be used to detect the existence of terephthalic acid in the presence of other acids. It forms beautiful flat prismatic crystals several inches long, which fuse at a temperature above 100° (Cent.), and sublime without decomposition. It is readily soluble in warm alcohol, and slightly soluble in cold alcohol.

The ethyl-terephthalic-ether forms long prismatic crystals resembling urea, and is readily soluble in cold alcohol.

The amyl-terephthalic-ether forms scaly crystals of pearly lustre, is readily soluble in alcohol, and fuses in the temperature of the hand.

Phenyl-terephthalic-ether, a white crystalline substance, fuses at above 100° C.

The acid compounds are generally formed in small quantities, along with the neutral ethers, by the action of the iodide of the alcohol radicals on terephthalate of silver. They are well-defined monobasic acids, and form crystallizable substances soluble in alcohol.

Nitro-terephthalic acid, $C^8 H^5 (NO^2) O^4$. This acid is formed by acting with a mixture of nitric and fuming sulphuric acid on terephthalic acid. When crystallized from certain solvents, it forms well-developed prismatic crystals of a faint yellow colour. From water, it deposits in cauliflower-like aggregations.

Nitro-terephthalic acid is readily soluble in warm alcohol and in warm water, and possesses the bibasic character of the terephthalic acid in a much higher degree. It forms well-defined crystallizable acid and neutral salts. The ethers of this acid are likewise crystal lizable. They differ, however, from the terephthalic acid ethers by their greater solubility in alcohol and their depressed fusing-point.

Chloride of terephthalyl ($C^8 H^4 O^2 Cl^2$) is obtained, together with oxychloride of phosphorus (hydrochloric acid being evolved), when terephthalic acid is acted upon with pentachloride of phosphorus at a temperature of 40° (Cent.). Chloride of terephthalyl is a solid and beautifully crystalline substance, without odour at the ordinary temperature, but evolving, when heated, a very pungent smell like that of chloride of benzoyl, which it resembles in all its reactions. With the alcohols it forms terephthalic ethers, with ammonia an amide, and with the organic bases compound amides. Terephthalyl-amide, $C^8 H^8 N^2 O^2$, can only be obtained by acting with chloride of terephthalyl on ammonia; it is a white amorphous substance insoluble in all solvents. Terephthalylamide, when treated with fuming nitric acid, yields nitro-terephthalic amide, $C^8 H^8 (NO^2) N^2 O^2$, which crystallizes in beautiful prisms.

Terephthalamide shows a remarkable resemblance to benzamide when treated with substances capable of abstracting the elements of water. It loses two equivalents of water ($H^2 O$), and is converted into terephthalylnitril, $C^8 H^4 N^2$. This remarkable substance is best formed by the action of anhydrous phosphoric acid on terephthalamide. It distils over in form of a liquid, which solidifies in the neck of the retort.

Terephthalylnitril is colourless and without odour, and forms beautiful prismatic crystals. It is insoluble in water, readily soluble in boiling alcohol, less soluble in cold alcohol, and insoluble in benzol. When boiled with caustic alkalies, it is gradually decomposed, ammonia is given off, and terephthalic acid is reproduced.

It is obvious that terephthalylnitril, like all similar substances, may be considered as a cyanogen compound, which in this instance would be the cyanide of the bibasic radical phenylen, $C^6 H^4$, which is not yet discovered. If we could succeed in obtaining phenylen, the artificial production of terephthalic acid or an isomeric would probably be attended with little difficulty.

By acting on nitro-terephthalic acid with reducing agents, it undergoes the same change as other nitro-compounds. The product of this reaction is the oxy-terephthalamic acid, or the analogue of the glycocoll of the formula $C^8 H^7 NO^4$. This new member of the glycocolls is a lemon-yellow substance, crystallizing in thin prismatic, and sometimes moss-like forms. It is very slightly soluble in cold water, alcohol, ether, and chloroform. Like other substances of this kind, terephthal-glycocoll combines with bases as well as with acids. The salts formed with the bases are crystalline; they are readily soluble in water and dilute alcohol, yielding colourless solutions of most remarkable fluorescent properties, which have been investigated by Professor Stokes.

The aqueous and alcoholic solution of the pure terephthalic glycocoll shows the same properties. The compounds with acids crystallize well, and if dissolved in a large quantity of water decompose. They do not possess the fluorescence when in their acid solution.

The ether-like compounds of oxy-terephthalamic acid are obtained by acting upon the corresponding ethers of the nitro-terephthalic acid with reducing agents. The methylic ether is a beautiful crystalline substance, readily soluble in warm alcohol, but much less soluble in any of the solvents than nitro-terephthalate of methyl. The ethylic ether crystallizes in large crystals with an appearance resembling those of nitrate of uranium. The solutions of this ether possess the fluorescent property in the highest degree. Oxy-terephthalamate of methyl and ethyl combine with acids and form well-defined salts. Oxy-terephthalamic acid, as well as its ether, are readily acted upon by nitrous acid, this reaction giving rise to a number of new derivatives, which vary in their nature according to the condition in which the reaction takes place.

M. Griess has lately made us acquainted with a new class of remarkable substances which are obtained by the action of nitrous acid on a certain class of nitrogenous bodies. The several derivatives he obtained by this reaction from oxy-benzamic acid have their representatives in the bibasic terephthalyl series, and are obtained with the utmost facility. On acting with nitrous acid upon an aqueous solution of the oxy-terephthalamic acid instead of an alcoholic solution, as is employed in Griess's reaction, this substance is readily decomposed, nitrogen is given off in large quantities, and there gradually separates

a whitish substance which is oxy-terephthalic acid, $C^8 H^6 O^5$. This acid is a substance of great interest, and its preparation offering much less difficulty than the analogous oxy-acids of the aromatic series, it affords an opportunity of studying to a fuller extent the nature of this class of acids, especially as it may be expected that the history of this acid will throw some light on the law of polybasicity. Oxy-terephthalic acid forms beautiful crystalline salts, which are less soluble than the corresponding terephthalates. The neutral ethers are liquid.

The chloride of oxy-terephthalyl is likewise a liquid readily decomposed by water and alcohols.

II. "Notes on the Generative Organs, and on the Formation of the Egg in the Annulosa."—Part I. By John Lubbock, Esq., F.R.S. Received February 5, 1861.

(Abstract.)

In the present paper I have communicated some observations on the Myriapoda, on *Petrobius*, and on certain Arachnida. Among the former I have examined species belonging to the genera *Glomeris*, *Iulus*, *Polydesmus*, *Lithobius*, *Cryptops*, *Geophilus*, and *Arthronomalus*. Through the labours of Brandt, Fabre, Newport, Stein, Treviranus, and other eminent naturalists, we are tolerably well acquainted with the anatomy of the generative organs in the Myriapods; but these observers have occupied themselves principally with the arrangement and forms of the organs, and have not paid much attention to the different stages of egg-development, nor to the relation in which the young egg stands to the surrounding tissues. This relation is indeed very curious, and seems to have been generally misunderstood. It is well known that there are in the Myriapods no long egg-tubes, as in most insects, but that each egg arises in a separate follicle. It was, however, natural to suppose that this follicle held the same position with reference to the ovary as the very similar egg-follicles of certain insects, as, for instance, of *Coccus*. This, however, is by no means the case. If we compare the ovary and egg-follicle of *Coccus* with the ovary and egg-follicle in *Glomeris*, we shall see that the egg-follicle is very much alike in both cases: the